

Exposure to Methyl *tert*-Butyl Ether and Benzene among Service Station Attendants and Operators

by Richard Hartle

Concerns for atmospheric pollution from auto exhaust have led to the blending of "oxygenates" with motor fuels. The most common oxygenate, methyl *tert*-butyl ether (MTBE) is currently required within several metropolitan areas (Denver and Phoenix) in the range of 12% of the motor fuel. Amendments to the Clean Air Act may expand this requirement to as many as 44 other areas of the United States in the near future. In consideration of the magnitude of potential uncontrolled exposures from its extensive use and a related concern involving the potential influence of MTBE blending on exposures to other constituents of gasoline (particularly benzene), an evaluation of exposures among service station attendants and operators was undertaken at the request, and in cooperation with, the American Petroleum Institute during the latter part of 1990. For application of the survey results to a broad audience, three categories or types of service stations were identified with regard to MTBE use and exposure potential: *a*) service stations that do not use MTBE or use it only as an octane enhancer, *b*) service stations with seasonal requirements to use 12-15% MTBE (the Denver, Colorado, and Phoenix, Arizona, metropolitan areas), and *c*) service stations equipped with stage II (active) vapor recovery systems (several coastal areas, most notably Southern California). At the two sampled service stations that use only minimal amounts of MTBE (less than 1%), only 1 of 32 personal breathing zone (PBZ) samples from attendants was above the analytical limit of detection, reported at 0.16 ppm. The geometric mean concentration of benzene among this same population ($n = 32$) was 0.04 ppm. At the two sampled stations with requirements to use oxygenated fuel, geometric mean MTBE and benzene concentrations were 0.30 and 0.04 ppm, respectively ($n = 41$). At the two stations equipped with stage II vapor recovery, 16 of 48 PBZ samples for MTBE were detectable, with a geometric mean concentration of 0.09 ppm. The geometric mean benzene concentration at these facilities was 0.06 ppm ($n = 48$).

Introduction

Concerns about atmospheric pollution caused by auto exhaust have led to the blending of "oxygenates" with motor fuels to reduce carbon monoxide emissions. The most common oxygenate, methyl *tert*-butyl ether (MTBE), is required within several metropolitan areas at levels of approximately 12% of the motor fuel. Amendments to the Clean Air Act may expand this requirement to as many as 44 U.S. metropolitan areas (1). Because of the large scope of potential exposures from its extensive use and because of a related concern involving the possible influence of MTBE blending on exposures to other constituents of gasoline (particularly benzene), an evaluation of exposures among service station attendants and operators was undertaken at the request of, and in cooperation with, the American Petroleum Institute (API) during the fall of 1990.

API conducted a parallel effort to determine community exposures at locations surrounding service stations and to

assess exposures to self-service customers at the same time as the National Institute for Occupational Safety and Health (NIOSH) evaluations (2). API's knowledge of NIOSH's previous evaluations of benzene/gasoline exposures (3) and interest in MTBE exposures resulting from its use as a gasoline additive prompted the joint evaluation concept. Under this concept, API contracted for the determination of gasoline exposures to self-service customers (breathing zone samples), plus community exposures via service station fence-line monitoring. Using these same sites, and during the same time period, NIOSH measured exposures to the service station attendants. This paper describes the NIOSH exposure assessment techniques and presents results of the personal (breathing zone) and bulk fuel samples collected for analysis of MTBE and benzene.

Methods

Site Selection

The purpose of the NIOSH evaluation was to determine the extent of exposure to selected gasoline components among service station attendants and operators. Service

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stations with at least one full-service island were evaluated to permit exposure monitoring of employees dispensing fuel. To permit extrapolation of the survey results to a wider population, three categories or types of service stations were identified with regard to MTBE use and exposure potential: *a*) stations that do not use MTBE or use it only as an octane enhancer (representing the vast majority of service stations in the United States), *b*) service stations with seasonal requirements to use 12–15% MTBE, and *c*) service stations equipped with phase II (active) vapor recovery systems (several coastal areas, most notably Southern California).

Cincinnati, Ohio, was selected to represent service stations that do not use MTBE or use it only as an octane enhancer. API-member oil companies identified two facilities in suburban Cincinnati based on relatively high levels of fuel sales. Similarly, two high-volume stations were selected in Phoenix, Arizona, because of the city's seasonal requirements for use of octane enhancers, such as MTBE, in motor fuels sold in the metropolitan area, and two service stations in Los Angeles were selected to determine exposures associated with the use of phase II vapor recovery systems.

To determine an appropriate sample size for acceptable precision in estimating mean exposure values, preliminary information and objectives of the evaluation were discussed with an NIOSH statistician. Based on an assumed coefficient of variation of approximately 39% (derived from results of the similar 1978 NIOSH study) (3), it was suggested that sampling consist of approximately 60 shifts, 2 samples/shift, with 16 sampled shifts from Cincinnati and 22 sampled shifts each from Phoenix and Los Angeles (R.W. Hornung, personal communication).

Sampling and Analytical Techniques

Environmental air samples for MTBE and benzene were collected on a primary tube containing 400 mg of activated charcoal followed by a backup tube containing 200 mg of charcoal. The sampling media were attached to the lapel of the worker in the area of their breathing zone. The samples were connected via flexible tubing to battery-operated pumps calibrated at flow rates of 0.1–0.5 L/min. Individual samples were collected for approximately 4 hr or two per 8-hr shift.

The charcoal tubes were analyzed by gas chromatography/flame ionization detection according to NIOSH Method 1615 (4). The analytical limit of detection (LOD) for MTBE ranged from 0.01 to 0.02 mg/sample and 0.002 to 0.03 mg/sample for benzene. This is equivalent to an LOD of approximately 0.03–0.25 ppm for MTBE and 0.01–0.40 ppm for benzene, depending on the sampled volume of air and the LOD at the particular analytical setting (4).

Other Measured Parameters

Several variables were measured during the environmental sample collection. These included: *a*) the liquid volume percent (LV%) of the target compounds in the gasoline, *b*) the amount of time the attendant spent in the

vicinity of the refueled vehicles, *c*) the number and size of spills occurring during the shift, and *d*) climatic conditions including wind speed, temperature, and relative humidity.

Bulk samples of the various grades of fuel were collected at the initiation of the site visit and several hours after each bulk fuel delivery (collection delayed to allow for mixing). Bulk analysis was similar to that of the charcoal tubes, except that samples were diluted and analyzed directly using gas chromatography/flame ionization detection according to NIOSH Method 1615. Weighted average LV% values were calculated for MTBE and benzene for each environmental sample by recording the amount of each grade of fuel dispensed by the attendant during the sample period. Also recorded was the amount of each grade of fuel dispensed at the entire station during the sample period.

The amount of time spent in the vicinity of the vehicle during refueling and the time actually spent at the nozzle was recorded during each sample period. If a spill occurred during refueling, its size was estimated (diameter) and recorded. A portable weather station was used to measure wind speed at each location. Measurements were logged on a strip chart recorder and averaged over the duration of the sampling shifts. Temperature and relative humidity were measured using a battery-operated psychrometer.

Results

Twenty-seven gasoline samples collected from the Cincinnati-area service stations revealed an average MTBE content ranging from 0.03 to 0.13 LV% with an average benzene content ranging from 0.39 to 0.86 LV% (average of nine sets of bulk samples with each set consisting of a sample from each grade of fuel; Table 1). The highest levels of MTBE and benzene were from a regular grade of gasoline, at 0.18 and 1.60 LV%, respectively. As expected, the average MTBE content of the gasoline samples collected in the Phoenix area was much higher ($n = 15$), ranging from 12.4 to 13.2% (highest MTBE level from a super-grade sample at 14 LV%). The average benzene content of these samples ranged from 1.18 to 1.63 LV% (highest at 1.9 LV%; regular and premium grades). Unexpectedly, the MTBE content of the premium-grade bulk samples collected from the Los Angeles area was as

Table 1. Average liquid volume percent.

City and grade	MTBE	Benzene
Cincinnati, OH		
Regular	0.13	0.86
Premium	0.12	0.78
Super	0.03	0.39
Phoenix, AZ		
Regular	12.4	1.63
Premium	13.0	1.31
Super	13.2	1.18
Los Angeles, CA		
Regular	0.07	1.76
Premium	0.03	1.76
Super	2.10	2.00

MTBE, methyl *tert*-butyl ether.

high as 11.0 LV% (average ranged from 0.03 to 2.10 LV%; $n = 33$). Because there are no requirements to use MTBE for control of carbon monoxide emissions in Los Angeles, we expected LV% levels in the same range as the Cincinnati fuel. Benzene content from the Los Angeles area samples ranged from 1.76 to 2.00 LV% (highest at 3.1 LV% from a super grade).

The Persian Gulf crisis had a major impact on the work practice parameters of the study. During the fall of 1990, fuel prices were increasing dramatically due to supply limitations imposed by the Gulf Crisis. Full-service prices tended to reflect this upward trend at an even higher rate. Because of this, even traditional full-service customers tended to purchase self-service fuel. Therefore, the work practice data (i.e., number of refuelings during a work shift and amount of fuel pumped), probably does not reflect the conditions typical of a stable fuel market. The exception was one station in Cincinnati that voluntarily furnished full-service refueling at self-service prices. This exception is reflected in the percent nozzle time values (percentage of shift spent pumping fuel) for the Cincinnati area as compared to the other two areas. At the Cincinnati stations, the average percentage of time during the sampling period actually pumping fuel was 11% (range 0.2–34%), while in Phoenix this value was 3.4% (range 0.3–24%) and in Los Angeles was 2.7% (range 0.1–6.9%). The average amount of fuel pumped during the sampling periods also was higher in Cincinnati, at 159 gallons, as compared to Phoenix (63 gallons) and Los Angeles (94 gallons).

Because of its potential influence on overall exposures to the fuel components, the number and size of fuel spills were recorded. Following are the results of these observations: Cincinnati averaged 1.9 spills at 3-in. diameter/sampling period, Phoenix averaged 0.9 spills at 4.5-in. diameter, and Los Angeles averaged 0.3 spills at 1.9-in. diameter.

MTBE and benzene exposure variations by location are depicted in Tables 2–4. Only one of 32 samples for MTBE collected in Cincinnati was above the analytical limit of detection at 0.16 ppm. This is indicative of the small amount of MTBE in this area's fuel (0–0.18 LV%). In Phoenix, where the MTBE content averaged 12.5–13 LV%, exposures averaged 0.30 ppm (geometric mean), ranging from 0.04 to 3.88 ppm (Table 3; range and geometric mean of 40 samples above the analytical limit of detection of 41 total samples collected). The Los Angeles (vapor recovery) MTBE exposures ranged from 0.02 to 0.73 ppm, averaging 0.14 ppm (Table 4; $n = 15$ detectable of 48 samples). As expected, the higher MTBE exposures were correlated with the service station distributing the premium-grade fuel containing 11 LV% MTBE.

Benzene exposures at the Cincinnati stations averaged 0.03 ppm, ranging from 0.01 to 0.29 ppm ($n = 28$ detect-

Table 2. Cincinnati exposure data for benzene.^a

Location	Mean	Minimum	Maximum
1 ($n = 16/16$)	0.08	0.02	0.29
2 ($n = 12/16$)	0.02	0.01	0.06
1 and 2 ($n = 28/32$)	0.03	0.01	0.29

^aMethyl *tert*-butyl ether not used in Cincinnati.

Table 3. Phoenix exposure data.

Location	Mean	Minimum	Maximum
MTBE			
1 ($n = 19/20$)	0.53	0.11	3.88
2 ($n = 21/21$)	0.17	0.04	2.12
1 and 2 ($n = 40/41$)	0.30	0.04	3.88
Benzene			
1 ($n = 19/20$)	0.08	0.02	0.52
2 ($n = 20/21$)	0.02	0.01	0.15
1 and 2 ($n = 39/41$)	0.05	0.01	0.52

MTBE, methyl *tert*-butyl ether.

Table 4. Los Angeles exposure data.

Location	Mean	Minimum	Maximum
MTBE			
1 ($n = 6/38$)	0.04	0.02	0.11
2 ($n = 9/10$)	0.21	0.21	0.73
1 and 2 ($n = 15/48$)	0.14	0.02	0.73
Benzene			
1 ($n = 20/38$)	0.08	0.04	0.19
2 ($n = 10/10$)	0.04	0.01	0.19
1 and 2 ($n = 30/48$)	0.06	0.01	0.19

MTBE, methyl *tert*-butyl ether.

able of 32 samples). In Phoenix, these exposures averaged 0.05 ppm, ranging from 0.01 to 0.52 ppm (39 detectable of 41 samples), and in Los Angeles, benzene exposures ranged from 0.01 to 0.19 ppm (30 detectable of 48 samples), averaging 0.06 ppm.

Conclusions

This study indicates that average occupational exposures to MTBE among service station attendants appear to be well below 1 ppm, even in areas with requirements for use of at least 12% MTBE in motor fuels. The geometric mean exposure determined from 41 samples collected in the Phoenix area was 0.3 ppm MTBE. Benzene exposure patterns appear to be similar to those previously determined by NIOSH in the 1970s (below 0.1 ppm). The average geometric mean exposures for Cincinnati, Phoenix, and Los Angeles were 0.03, 0.05, and 0.06 ppm, respectively. Preliminary statistical analysis of this data indicates that addition of as much as 13% MTBE does not have a significant effect on benzene exposures.

It is interesting to note that of the three regions studied, average benzene exposures at service stations equipped with vapor recovery systems were equivalent to exposures measured at the other stations. Preliminary statistical analyses indicates that even if the other work practice and site-specific variables are controlled (i.e., amount of fuel pumped, amount of benzene in the fuel, etc.) vapor recovery has no significant effect on reducing exposures to benzene among the attendants.

We are currently analyzing the data for significant relationships between exposures to MTBE and benzene and work practice, site-specific, and climatic parameters. This analysis will enable us to construct predictive models

of exposure given a set of known variables (MTBE/benzene content, work practices, etc.), thus allowing more meaningful recommendations toward reducing exposures.

REFERENCES

1. Ainsworth, S. J. Booming MTBE demand draws increasing number of producers. *Chem. Eng. News* 69: 13–16 (1991).
2. Clayton Environmental Consultants. Gasoline Vapor Exposure Assessment for the American Petroleum Institute (API). Contract Report No. 31774.00 for API. Clayton Environmental Consultants, Inc., Pacific Operations, Los Angeles, CA, 1991.
3. Hartle, R. W. Occupational Exposure to Benzene at Automotive Service Stations (Thesis). Department of Public Health, University of Washington, Seattle, WA, 1980.
4. NIOSH Methyl tert-Butyl Ether. In: NIOSH Manual of Analytical Methods. 4th rev. ed. (P. M. Eller, Ed.), DHHS (NIOSH) Publication No. 90-121, National Institute for Occupational Safety and Health, Washington, DC, 1991.